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Chiral diketopyrrolopyrrole-helicene polymer with efficient red circularly polarized luminescence

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Keywords: helicene, diketopyrrolopyrrole, circularly polarized luminescence, red emitters, exciton coupling, chiral polymers

Abstract

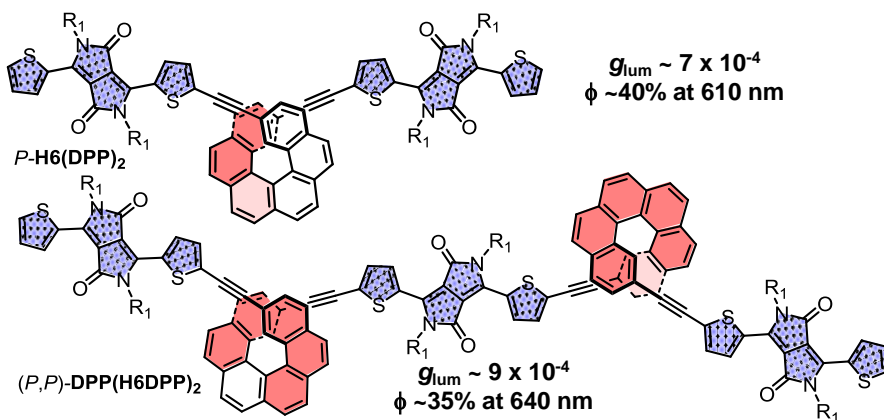
Chiral diketopyrrolopyrrole (DPP)-helicene polymers were synthesized to develop efficient red circularly polarized (CP) light emitters. These original chiral dyes display intense electronic circular dichroism (ECD) and CP luminescence (CPL) in the far-red spectral region owing to the presence of excitonic coupling between achiral DPP within the chiral environment of the polymeric structure. This work affords an interesting example illustrating the potential of π -conjugated helical polymers for chiral optoelectronic applications.

1 Introduction

Circularly polarized (CP) light has received renewed attention owing to its superior potential over unpolarized one in a diverse range of domains such as (chir)optoelectronics (stereoscopic displays, organic light-emitting diodes (OLEDs), optical information processing, etc.) as well as in bio-imaging and chiral sensing (Berova et al., 2000; Berova et al., 2012; Riehl and Richardson, 1986; Maeda and Bando, 2013; Kumar et al., 2015; Hiroki et al., 2018; Longhi et al., 2016; Francesco and Lorenzo, 2015; de Bettencourt-Dias, 2014; Carr et al., 2012; Zinna et al., 2015; Brandt et al., 2016, Zinna et al., 2017; Zinna and Di Bari 2018; Han et al., 2018; Meng et al., 2017). Until recently, luminescent chiral lanthanides complexes have been the most studied molecular CPL emitters since this family of compounds can display relatively high level of circularly polarized emission,

characterized by a luminescence dissymmetry factor $g_{\text{lum}} = 2(I_L - I_R)/(I_L + I_R)$, of more than 1 (Carr et al., 2012; Zinna et al., 2015; Zinna and Di Bari, 2018). However, lanthanide complexes often possess low luminescent quantum yield (ϕ) and stability issues, which may difficultly render their integration in optoelectronic devices such as CP-OLEDs, chiral photovoltaics and transistors for example. To circumvent these aspects, the development of chiral emitting small organic molecules (SOM) has gained increasing interest, also benefiting from their tunable photophysical and chiroptical properties from the blue to the near-infrared spectral region (Carr et al., 2012; Zinna et al., 2015; Zinna and Di Bari, 2018). One particularly appealing synthetic strategy to design efficient CPL emitters has consisted in developing chirally perturbed π -extended achiral chromophores, mostly based on C_2 -symmetric chiral moieties (chiral binaphthyl or 1,2-diamino-cyclohexane derivatives) linked to bodipy or perylene organic dyes (Kumar et al., 2013; Kumar et al., 2014; Sheng et al., 2016; Tsumatori et al., 2010; Kumar et al., 2015; Langhals et al., 2011; Sánchez-Carnerero et al., 2014). In addition, helicenes have recently shown to be very good scaffolds for the development of emissive materials with strong CPL activity (Chen and Shen, 2016; Gingras, 2013; Dhbaibi et al., 2018; Dhbaibi et al., 2020; Zhao et al., 2019; Shen et al. 2020). Following this approach, we recently reported helical π -conjugated helicene-diketopyrrolopyrrole (DPP) dyes (*P*-**H6(DPP)**₂ and (*P,P*)-**DPP(H6DPP)**₂, Figure 1) (Dhbaibi et al., 2018) as red CPL emitters, (Nishimura et al., 2017; Sakai et al., 2016, Pascal et al., 2016; Shen et al., 2014; Saleh et al., 2015; Biet et al., 2017) arising from an intramolecular exciton coupling (Harada et al., 2012) between the achiral DPP units placed within the chiral environment of the helicene. Based on purely π - π^* transitions, this design afforded promising g_{lum} factors of $6\text{--}9 \times 10^{-4}$ at 610–650 nm associated with fluorescence quantum yields (ϕ) of 35–40 %. To our knowledge, this study remains the only example of DPP based CPL emitters, despite the promising potential of diketopyrrolopyrrole and its derivatives in a broad range of applications such as OLEDs, photovoltaic devices, organic transistors, and fluorescent probes (Data et al., 2016; Kaur and Choi, 2015; Heyer et al., 2015; Nielsen et al., 2013; Grzybowski and Gryko, 2015).

Previous work: Chiral exciton coupling of achiral DPP (Dhbaibi et al., 2018)



This work: Helical polymer DPP based CPL emitters

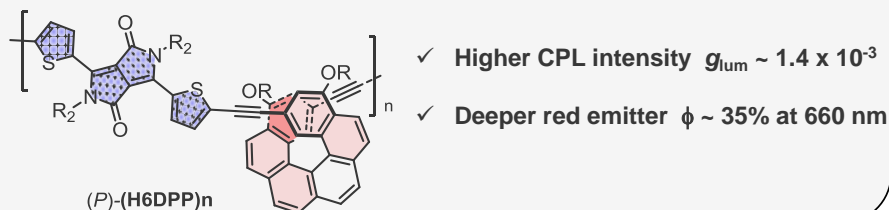


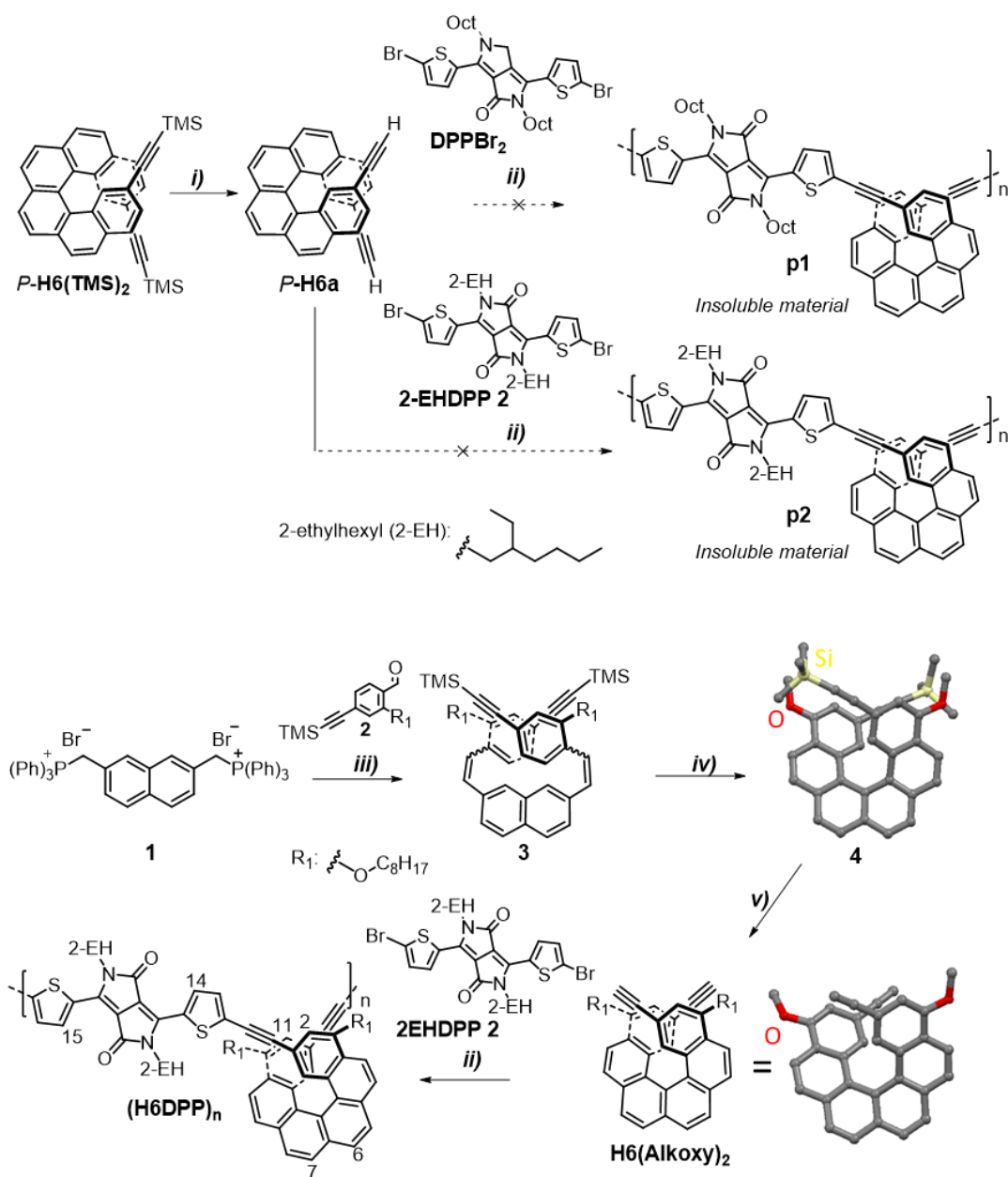
FIGURE 1. Chemical structures of CPL emitters based on helicene-diketopyrrolopyrrole polymers and their corresponding polarized and unpolarized luminescence characteristics (*P* enantiomers are shown).

With the aim of deeper exploring this innovative and promising synergy between chiral helicene and achiral diketopyrrolopyrrole dye, we report here the synthesis and chiroptical properties of novel π -conjugated helical polymeric CPL emitters, namely *rac*-, (*P*)- and (*M*)-(**H6DPP**)_n, Figure 1. These new examples of helicene-diketopyrrolopyrrole association displays intense electronic circular dichroism (ECD) in the visible region and strong red CPL with $g_{\text{lum}} = 1.4 \times 10^{-3}$ at 660 nm, associated with a high ϕ of ~35 %. This first example of chiral helicene-DPP based polymer exhibits higher CPL response than the molecular chiral helicene-DPP dyes previously reported, and brings interesting aspects for the design of efficient polymeric red and near infra-red CPL emitters.

Results and discussion

Synthesis of polymer (**H6DPP**)_n

The helicene-DPP polymers were prepared using the Sonogashira coupling between a helicene decorated with two alkynyl functions and a DPP core substituted with two bromothiophene units. In a first attempt to synthesize polymer (**H6DPP**)_n, the coupling was performed using enantiopure *P*- and *M*-2,15-bis-(ethynyl)[6]helicene (*P*- and *M*-**H6a**) (Anger et al., 2012) with 3,6-bis(5-bromothiophen-2-yl)-2,5-diketopyrrolopyrrole, **DPPBr**₂, respectively (Figure 2, where only *P* enantiomer is described) (Wu et al., 2015). While the reactions seemed to proceed efficiently, they resulted in the formation of insoluble dark blue material (**p1**, Figure 2). To circumvent this solubility issue, we introduced widely used branched 2-ethylhexyl (2-EH) chains on the DPP unit in place of the linear octyl ones (Palai et al., 2010; Huo et al., 2009). Although this fragment has a chiral center, we used its racemic form since a weak influence of these additional stereogenic centers is expected on the photophysical and chiroptical properties of the final polymer in diluted solution. Unfortunately, this new approach also afforded insoluble blue solid when a stoichiometric mixture of *P*-**H6a** and **2EHDPP 2** was subjected to the Sonogashira coupling conditions (**p2**, Figure 2). To further increase the solubility of the obtained polymer material, the helicenic fragment was also functionalized with additional linear octyloxy chains through a new synthetic pathway involving 2-(octyloxy)-4-((trimethylsilyl)ethynyl)benzaldehyde, **2**, as starting material for the synthesis of the helicene fragment. Indeed, the latter was engaged in a double Wittig reaction with naphthyl-2,7-dimethylphosphonium bromide salt, **1**, to give 2,7-bis(2-(octyloxy)-4-((trimethylsilyl)ethynyl)styryl)naphthalene, **3**, in 60% yield. The resulting *cis/trans* stilbene mixture was subsequently submitted to a photocyclisation reaction with propylene oxide as an acid scavenger to afford *rac*-2,15-bis-((trimethylsilyl)ethynyl)-4,13-bis-(octyloxy)[6]helicene (**4**) in 50% yield, followed by deprotection reaction of the two remaining TMS groups to yield **H6(Alkoxy)**₂ (Scheme 1). Fully characterized by NMR spectroscopy and mass spectrometry (see ESI), the structures of the two latters were further ascertained by X-ray crystallographic analysis (see Scheme 1 and ESI). Both *rac*-**4** and *rac*-**H6(Alkoxy)**₂ crystallized in a *P*-1 space group and displayed helicity (dihedral angle between the two terminal rings) of 41.1° and 54.4°, respectively, which is in the range of classical carbo[6]helicenes (Chen and Shen, 2016; Gingras, 2013; Dhbaibi et al., 2019). Moreover, the lateral octyloxy chains point toward the outside of the molecules, which may disfavor the formation of polymer aggregates in solution.



104

105 **FIGURE 2.** Synthesis of enantiopure $P\text{-(H6DPP)}_n$. TMS: trimethylsilyl. Reaction conditions: *i*)
 106 TBAF, CHCl_3 ; *ii*) $\text{Pd(PPh}_3)_4$, CuI, Et_3N /toluene, 50°C ; *iii*) $n\text{-BuLi}$, THF, -78°C to rt, 60%; *iv*) $h\nu$, I_2
 107 (1 equiv.), propylene oxide (50 equiv.), toluene, 50%; *v*) TBAF, CHCl_3 , 52%, chiral HPLC. X-ray
 108 crystal structures of *rac*-**4** and *rac*-**H6(Alkoxy)**₂ (octyl chains and hydrogen atoms have been omitted
 109 for clarity).

110 *Rac*-**H6(Alkoxy)**₂ was then submitted to chiral HPLC separation to give *P*-(+) and *M*-(-) in 99% and
 111 98.5% of *ee*, respectively (see ESI for detailed experimental conditions). These enantiomers, as well
 112 as the racemic compound, were finally engaged in the polymerization reaction with **2EHDPP 2** and
 113 gave expected soluble polymers which were firstly filtered over a silica plug, then further purified by
 114 size-exclusion chromatography (SEC, CHCl_3) before precipitated using $\text{CHCl}_3/\text{MeOH}$ solvent
 115 mixture to yield *P*-, *M*- and *rac*-(**H6DPP**)_n in approximately 45% yield for each polymer (see ESI).
 116 These novel chiral dyes are soluble in common organic solvents such as THF, CHCl_3 , and CH_2Cl_2 ,
 117 and were characterized by ^1H NMR and SEC using a polystyrene standard in THF. The obtained

NMR spectrum displays characteristic signals for both helicene and DPP starting materials: for instance, shielded H^{2,11} and deshielded H^{6,7} helicenic protons at 6.75 and 8.50 ppm respectively, and deshielded DPP protons H^{14,15} at 9.10 ppm (see ESI). The number average molecular mass (M_n) for *rac*-, *P*-, and *M*-(**H6DPP**)_n were estimated to be 6.9×10^3 , 5.3×10^3 and 6.4×10^3 , respectively, which correspond to a low degree of polymerization, *ca.* 5-6 (helicene-DPP) units (See ESI). The thermal stability of *rac*-(**H6DPP**)_n was also evaluated by thermogravimetric analysis (TGA) and resulted in an onset decomposition temperature at 300 °C with a 10% weight loss.

UV-Vis, ECD and electrochemical characterizations

The ground state photophysical and chiroptical properties of DPP-helicene polymers were investigated in CH₂Cl₂ solutions and compared with corresponding precursors and previously reported **DPP(H6DPP)**₂. UV-Vis spectrum of (**H6DPP**)_n polymer displays two main absorption signatures between 300 and 425 nm and between 530 and 675 nm that correspond to a combination of helicene and DPP transitions for the higher energy region and only from DPP transitions for the low energy part. The latter absorption region is red-shifted by 70 nm in comparison with DPP precursor, characterized by $\epsilon = 7.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 565 nm and $35 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 635 nm for **2EHDPP 2** and (**H6DPP**)_n, respectively, resulting from the extension of the π -conjugation via the alkynyl bridges between the DPP dye and the helicene units. These observations are supported by comparison with **DPP(H6DPP)**₂ UV-vis spectrum, where contributions of both “DPP-helicene” and “helicene-DPP-helicene” fragments are superposed in the red region (see ESI for additional details). Going from oligomer **DPP(H6DPP)**₂ to polymer (**H6DPP**)_n does not strongly red-shift the overall absorption signature ($\lambda_{\text{max}} = 620$ and 635 nm for **DPP(H6DPP)**₂ and (**H6DPP**)_n lowest absorption bands, respectively), which suggests that electronic communication between each bis(ethynyl)DPP unit through the π -conjugated helicene is relatively limited along the polymer. The observed difference of 15 nm results probably from the presence of the electron donating octyloxy groups on the helicene fragment for (**H6DPP**)_n.

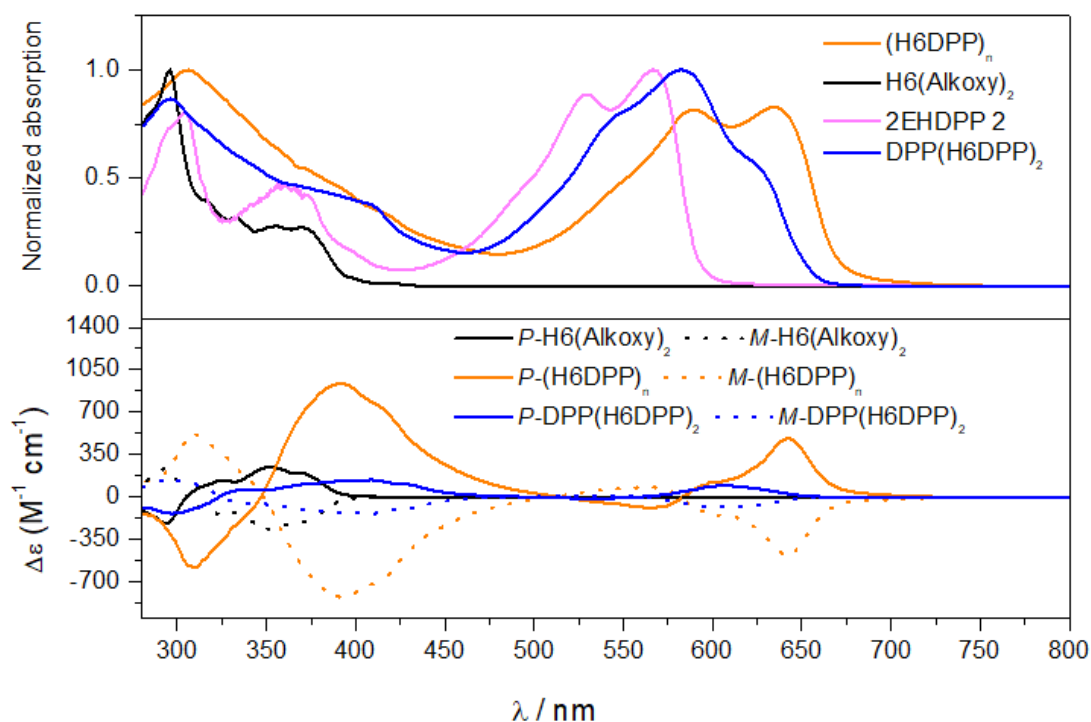
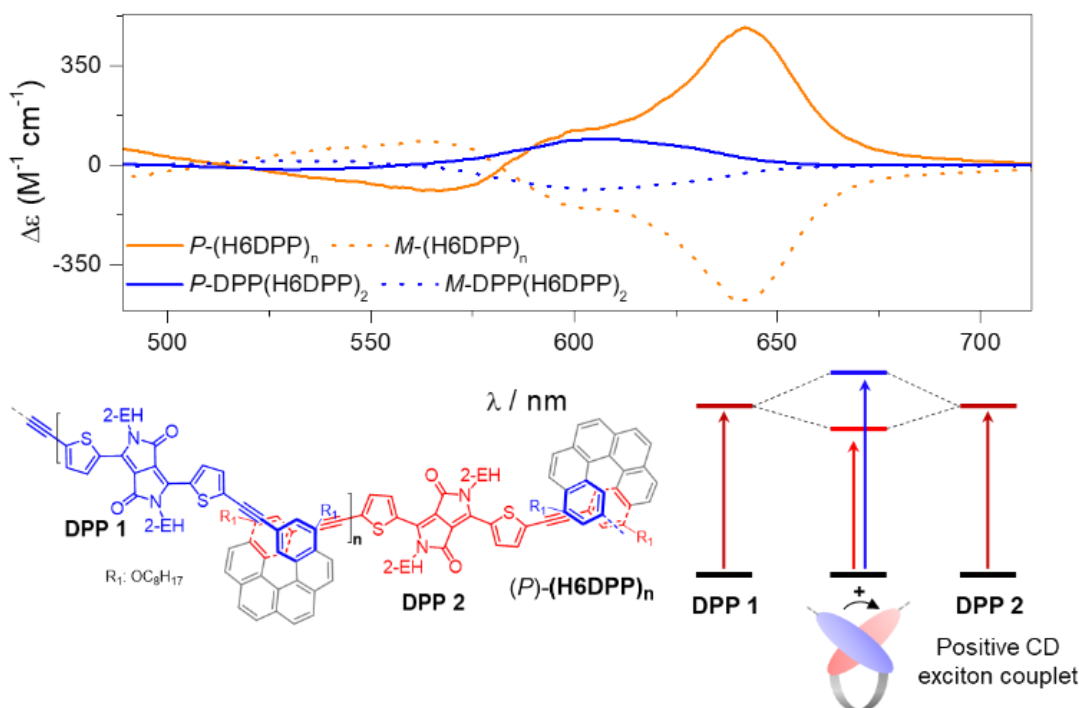


FIGURE 3. UV-vis (top) and ECD (bottom) spectra of **H6(Alkoxy)₂** (black), **2EHDPP 2** (purple), **DPP(H6DPP)₂** (blue) and **(H6DPP)_n** (orange) in CH₂Cl₂ at 298 K ($\sim 10^{-5}$ M).

ECD of *P*- and *M*-(**H6DPP**)_n displays expected mirror-image spectra with intense responses ranging from 280 to 700 nm (Figure 3). *P*-(**H6DPP**)_n exhibits an intense negative ECD band ($\Delta\epsilon = -576 \text{ M}^{-1} \text{ cm}^{-1}$) at 309 nm which is 19 nm red-shifted compared to helicene *P*-**H6(Alkoxy)₂**, a broad strong positive band between 347 and 500 nm with a maximum at 391 nm ($\Delta\epsilon = +940 \text{ M}^{-1} \text{ cm}^{-1}$) and a shoulder at 414 nm ($\Delta\epsilon = +740 \text{ M}^{-1} \text{ cm}^{-1}$), a negative contribution at 565 nm ($\Delta\epsilon = -88 \text{ M}^{-1} \text{ cm}^{-1}$) followed by a positive one with a maximum at 640 nm ($\Delta\epsilon = +481 \text{ M}^{-1} \text{ cm}^{-1}$). This lowest bisignate DPP-centered signal is clearly reminiscent of what we observed for *P,P*-**DPP(H6DPP)₂** (Figure 4), which was attributed to a chiral excitonic coupling between the DPP-centered π -orbitals in the helical arrangement (Dhbaibi et al., 2018; Bouvier et al., 2018; Dhbaibi et al., 2020). Elongating the number of helicene-DPP association within polymer *P*-(**H6DPP**)_n appears as an efficient strategy to obtain very intense ECD signature across the whole spectrum and especially in the red region thanks to the increase of the excitonic coupling intensity. Indeed, this higher sensitivity to red circularly polarized light for *P*-(**H6DPP**)_n is confirmed by the evaluation of the associated dissymmetry factor $g_{\text{abs}} = \Delta\epsilon/\epsilon = +1.8 \times 10^{-3}$ at 649 nm, i.e. a 40 % increase in comparison with *P,P*-**DPP(H6DPP)₂** ($g_{\text{abs}} = +1.3 \times 10^{-3}$ at 610 nm).



161 **FIGURE 4.** Enlargement of 490-710 nm region of the ECD spectra of **DPP(H6DPP)₂** (blue) and
 162 **(H6DPP)_n** (orange) in CH₂Cl₂ at 298 K (~10⁻⁵ M), with schematic illustration of the chiral exciton
 163 coupling process in **(H6DPP)_n**.

164 The electrochemical behavior of **(H6DPP)_n** was investigated by cyclic voltammetry (CV, Figure
 165 S17, Table S1), which displays pseudo-reversible oxidation process at ca. +0.81 V and a reversible
 166 reduction one at -1.24 V vs. SCE, respectively assigned to the oxidation and the reduction of the DPP
 167 unit(s). The calculated HOMO and LUMO energy level were -5.21 eV and a LUMO level of -3.16
 168 eV, respectively, leading to an estimated electrochemical band gap of 2.05 eV.

169 Unpolarized (PL) and circularly polarized luminescence (CPL)

170 To our delight, **(H6DPP)_n** displays intense unpolarized vibronic emission arising from the DPP-
 171 ethynyl fragment with a maximum intensity at 660 nm and a quantum yield of 35 %. Interestingly,
 172 these values suggest that embedding DPP-helicene fragment within a polymer material is also an
 173 efficient strategy to make deeper red emitter while keeping a high fluorescence efficiency since
 174 **DPP(H6DPP)₂** exhibits similar luminescence quantum yield ($\phi = 35\%$) but its emission is blue
 175 shifted ($\lambda_{\text{max}} = 650$ nm). In order to rule out the possibility of charge transfer character the emission
 176 of the polymer was carried out in solvents of different polarity including toluene, tetrahydrofuran and
 177 dichloromethane in which the polymer was fully soluble (Figure S13). A similar spectral behavior
 178 was found in these solvents with a structured signals and no significant shift of the emission spectra,
 179 indicating that the nature of the emission is mainly based on π - π^* transitions localized on the DPP
 180 units. The fluorescence kinetics of the polymer was also performed at 650 nm (Figure S14) and
 181 nicely fits a single-exponential decay function with a decay time constant of 2.08 ns.

182 Regarding circularly polarized luminescence (CPL), mirror-image spectra were also obtained for *P*-
 183 and *M*-**(H6DPP)_n** with a maximum and a structural signature similar to unpolarized emission,
 184 highlighting the synergy of the DPP-helicene association also in the polymer chiral excited-state
 185 (Figure 5). Moreover, g_{lum} factor of $+1.3 \times 10^{-3}$ was determined for *P*-**(H6DPP)_n**, which suggests a

relatively similar chiral geometry of the ground and emitting excited states ($g_{\text{lum}}/g_{\text{abs}} = 0.72$) and represents also a *ca.* 40 % increase in comparison with *P,P*-DPP(H6DPP)₂ ($g_{\text{lum}} = +0.9 \times 10^{-4}$). The obtained g_{lum} values for polymers (H6DPP)_n are in the same range of reported SOM CPL emitters ($10^{-4} - 10^{-2}$), and are among the most efficient ones for the far red and near infrared region (*i.e.* for $\lambda_{\text{max}} > 650 \text{ nm}$, $3 \times 10^{-4} < g_{\text{lum}} < 4.3 \times 10^{-3}$) (Hiroki et al., 2018).

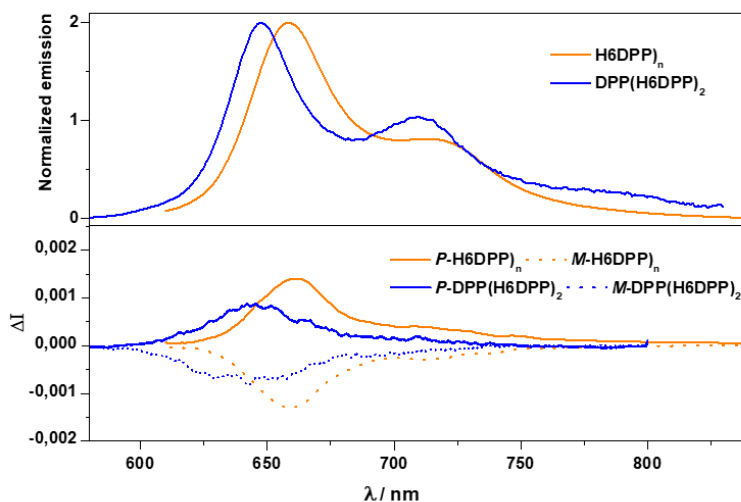


FIGURE 5. Normalized fluorescence (top) and CPL (bottom) spectra of DPP(H6DPP)₂ (blue) and (H6DPP)_n (orange) in CH₂Cl₂ at 298 K. CPL spectra for *P* and *M* enantiomers are shown respectively in solid and dotted lines.

Conclusions

In summary, we have successfully prepared novel helical conjugated polymers based on the association between enantiopure carbo[6]helicene derivative and diketopyrrolopyrrole dye via the Sonogashira cross-coupling. These polymers show strong ECD signal in the visible region ($\Delta\epsilon = 482 \text{ M}^{-1} \text{ cm}^{-1}$ at 642 nm, for *P*-(H6DPP)_n) and strong CPL emission response signals ($g_{\text{lum}} = +1.3 \times 10^{-3}$ at 662 nm) along with high fluorescence quantum efficiency ($\phi_f = 35 \%$). Extending the efficiency of exciton coupling process in chiral polymers allow efficient preparation of CPL emitters deeper in the red and near-infrared region. Our results provide an alternative approach to the metalation and the push-pull functionalization methodologies to extended and to improve the chiroptical responses of the helicene molecules by taking advantages of the strong synergy between the chiral environment controlled by the helicene center and the interesting photophysical properties offered by the corresponding dye. The polymers based on the helicene unit that we presented in this work can be used as a new class of candidates for efficient CPL materials in optoelectronics and bioimaging applications.

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2 Author Contributions

Kais Dhbaibi and Chengshuo Shen synthesized and characterized the molecules; Marion Jean and Nicolas Vanthuyne performed the HPLC resolution; Thierry Roisnel performed the X-ray analysis; Marcin Górecki performed CPL measurements; Bassem Jamoussi, Ludovic Favereau and Jeanne Crassous supervised the work, analyzed the results and wrote the manuscript.